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THE SYNTHESIS OF SOME MIXED ESTERS OF DITHIOPHOSPHORIC ACID

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Mixed esters of thiophosphoric acids attracted the attention of many investigators in recent years, because some compounds of this type were useful in agriculture in the fight against plant pests (1-5).

Some esters of dithiophosphoric seem interesting in this respect, even though they are less active than thiophosphoric acid esters.

Only a few methods are described for obtaining esters of dithiophosphoric acid, the most important of which is the reaction between salts of dialkyldithiophosphoric acid and halogen derivatives (6, 7):

$$(RO)_2PS_2Na + R^1X \rightarrow (RO)_2PS_2R^1 + NaX$$

The majority of the mixed esters of dithiophosphoric acid known at present were prepared in this way. However, this method gives good yields only when the halogen atom in the halogen derivative is sufficiently mobile.

It seemed of interest to us to study the reaction of the addition of dialkyldithiophosphoric acid to the double bond of unsaturated compounds, clarifying the possibility of obtaining mixed esters of dithiophosphoric acid in this manner. Such an addition of dialkylphosphorous acids to unsaturated compounds was successfully accomplished recently by A. N. Pudovik and B. A. Arbuzov (8-12).

As a result of experiments carried out in the beginning of 1951, it was possible to establish that the reaction between dialkyldithiophosphoric acid and unsaturated compounds follows the scheme:

$$(RO)_2PS_2H + >C=C< \rightarrow (RO)_2PS_2-\overset{|}{C}-\overset{|}{C}-H$$

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The yield of mixed esters of dithiophosphoric acid by this method is very satisfactory. In the presence of solid potassium hydroxide, the reaction proceeds in the cold. We studied the reaction between dialkyldithiophosphoric acid and styrene, methyl acrylate, acrylonitrile, vinyl acetate, acroleine, esters of maleic acid, and some other compounds. The compounds thus obtained and their properties are listed in the appended table.

It is necessary to note that in 1952 a report appeared (13) describing the use of the above reaction for the synthesis of esters of dithiophosphoric acid, which prompted us to publish the present research. It should be noted that the addition reaction of dialkyldithiophosphoric to unsaturated compounds was studied by us on 31 examples, while the American authors cited only six instances.

Experimental Part

The preparation of mixed esters of dithiophosphoric acid from practically all of the compounds was carried out under the following standard conditions: to one mole of olefin, one mole of dialkyldithiophosphoric acid was gradually added with constant stirring. The addition was done at such a rate that the temperature of the reaction mixture did not exceed 40-45°. After addition of the entire amount of dialkyldithiophosphoric acid to the reaction mixture, the mixture was left standing at room temperature until the amount of free dialkyldithiophosphoric acid no longer changed. The dialkylthiophosphoric acid was determined in special samples by titrating with 0.1 N KOH. The unreacted olefin was then distilled from the reaction mixture and the remainder was fractionated under vacuum.

The dialkyldithiophosphoric acid was obtained by the interaction of pentavalent phosphorus with the corresponding alcohol (14).

Mixed Esters of Dithiophosphoric Acid

Initial Compounds: Dialkyldithiophosphoric Acid	Initial Compounds: Olefin	Yield (%)	Temp (deg) and Pressure (mm)	n_D^{20}	d_4^{20}	Phosphorus Content of Product: Calculated	Phosphorus Content of Product: Found
$(CH_3O)_2PS_2H$	$CH\text{-}COOC_2H_5$ // $CH\text{-}COOC_2H_5$	50	160-170/3.5	1.4960	1.2076	9.36	8.95 8.5
$(C_2H_5O)_2PS_2H$	$CH\text{-}COOC_2H_5$ // $CH\text{-}COOC_2H_5$	59	157-162/3	1.4910	1.1742	8.65	8.62 8.5
$(C_3H_7O)_2PS_2H$	$CH\text{-}COOC_2H_5$ // $CH\text{-}COOC_2H_5$	27	145/0.1	1.4880	1.1706	8.03	8.3 8.42
$(i\text{-}C_2H_7O)_2PS_2H$	$CH\text{-}COOC_2H_5$ // $CH\text{-}COOC_2H_5$	39	151/4	1.5440	1.0702	8.03	8.32 8.3
$(C_4H_9O)_2PS_2H$	$CH\text{-}COOC_2H_5$ // $CH\text{-}COOC_2H_5$	40	125-128/0.025	1.4861	1.1078	7.5	7.72 7.92
$(i\text{-}C_4H_9O)_2PS_2H$	$CH\text{-}COOC_2H_5$ // $CH\text{-}COOC_2H_5$	15	117-130/0.04	1.4855	1.0642	7.5	7.94 7.84
$(C_2H_5O)_2PS_2H$	$CH_2=CH\text{-}CN$	33	137-142/3.5	1.5195	1.1704	13.09	12.75 12.88
$(C_3H_7O)_2PS_2H$	$CH_2=CH\text{-}CN$	30	116-120/0.05	1.5068	1.0505	11.7	11.71 11.98

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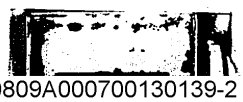

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$(C_4H_9O)_2PS_2H$	$CH_2=CH-CN$	27.5	121-3/0.03	1.5050	1.0816	10.5	10.51 10.62
$(i\text{-}C_4H_9O)_2PS_2H$	$CH_2=CH-CN$	44	122-3/0.05	1.5010	1.0986	10.5	10.81 11.0
$(CH_3O)_2PS_2H$	$CH_2=CH-COOCH_3$	38	100-103/2	1.5252	1.1558	12.71	13.3 13.4
$(C_2H_5O)_2PS_2H$	$CH_2=CH-COOCH_3$	71	115-7/1.5	1.4948	1.1517	11.4	11.37 11.34
$(C_3H_7O)_2PS_2H$	$CH_2=CH-COOCH_3$	46	80-81/0.05	1.5075	1.0984	12.85	12.9 13.0
$(i\text{-}C_3H_7O)_2PS_2H$	$CH_2=CH-COOCH_3$	50	72-74/0.1	1.4335	1.846	10.32	10.9 10.84
$(i\text{-}C_4H_9O)_2PS_2H$	$CH_2=CH-COOCH_3$	43	104/0.075	1.4858	1.0926	9.43	9.96 10.1
$(C_4H_9O)_2PS_2H$	$CH_2=CH-COOCH_3$	25	109/0.4	1.4915	1.0915	10.91*	10.22 10.48
$(CH_3O)_2PS_2H$	$CH_2=CH-C_6H_5$	50	128-132/0.45	1.5705	1.2108	11.82	11.5 11.65

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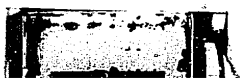

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$(C_2H_5O)_2PS_2H$	$CH_2=CH-C_6H_5$	35	135-137/0.15	1.5498	1.1444	10.67	11.0 11.28
$(C_3H_7O)_2PS_2H$	$CH_2=CH-C_6H_5$	28	129-131/0.1	1.5381	1.0990	9.73	9.82 9.92
$(i\text{-}C_3H_7O)_2PS_2H$	$CH_2=CH-C_6H_5$	38.5	121-124/0.2	1.5365	1.0966	9.73	9.81 9.95
$(C_4H_9O)_2PS_2H$	$CH_2=CH-C_6H_5$	13	137-140/0.025	1.5320	1.0890	8.94	8.82 8.8
$(i\text{-}C_4H_9O)_2PS_2H$	$CH_2=CH-C_6H_5$	17.5	117-122/0.04	1.5301	1.0860	8.94	9.1 9.18
$(CH_3O)_2PS_2H$	$CH_2=CH-COOCH_3$	67	145/3	1.5160	1.2625	12.69	12.71 12.78
$(C_2H_5O)_2PS_2H$	$CH_2=CH-COOCH_3$	83	167/1.5	1.5050	1.1911	11.38	11.92 11.98
$(i\text{-}C_4H_9O)_2PS_2H$	$CH_2=CH-COOCH_3$	58	124-129/0.2	1.4915	1.1162	9.43	9.62 9.72
$(CH_3O)_2PS_2H$	$CH_2=C(CH_3)-COOCH_3$	38	133-135/2	1.5100	1.2330	12.01	12.01 11.8

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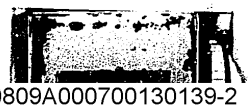
$(C_2H_5O)_2PS_2H$	$CH_2=C(CH_3)-COOCH_3$	59	154.5/5	1.4995	1.1577	10.95	11.31 11.35
$(i\text{-}C_3H_7O)_2PS_2H$	$CH_2=C(CH_3)-COOCH_3$	47	84-85/0.02	1.4935	1.1203	9.84	10.15 10.28
$(i\text{-}C_4H_9O)_2PS_2H$	$CH_2=C(CH_3)-COOCH_3$	56	115-116/0.04	1.4915	1.1138	9.05	9.32 9.16
$(C_4H_9O)_2PS_2H$	$CH_2=C(CH_3)-COOCH_3$	38	110/0.025	1.4918	1.1132	9.05	8.8 9.14
$(i\text{-}C_3H_7)_2PS_2H$	$CH_2=CHCHO$	37	74/0.15	1.5040	1.1348	11.5	11.9 11.28

* This product decarboxylizes during distillation; the phosphorus content is computed on the basis of the decarboxylated ester.



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